

Sm and Gd isotopic measurements in test samples for the MUSES-C mission

By

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(1 February 2003)

Abstract: The procedures for separation of Sm and Gd by resin chemistry were established, and then Sm and Gd isotopic measurements in two test samples 1F and 2F were performed to study the exposure records. Significant isotopic deviations over the analytical accuracy were not observed in ^{149}Sm - ^{150}Sm and ^{157}Gd - ^{158}Gd of the two samples. The estimated neutron fluences of 1F and 2F were $(0 \pm 2.2) \times 10^{15}$ and $(0.8 \pm 3.1) \times 10^{15}$ n/cm², respectively.

1. INTRODUCTION

Thermalized neutrons are produced by the interaction of cosmic rays with planetary materials. Isotopes having large neutron capture cross sections in planetary materials are affected by the secondarily arising neutrons. Because ^{149}Sm , ^{155}Gd and ^{157}Gd have extraordinarily large neutron capture cross sections, the isotopic shifts of ^{149}Sm - ^{150}Sm , ^{155}Gd - ^{156}Gd and ^{157}Gd - ^{158}Gd have been used to study the exposure records of planetary materials. Up to the present, we have established the analytical technique to measure isotopic compositions of Sm and Gd in geological samples (Hidaka et al., 1995) and applied it for meteorites (Hidaka et al., 1999; 200a), lunar samples (Hidaka et al., 200b), and terrestrial uranium minerals (Hidaka and Gauthier-Lafaye, 2001). This technique may be useful to study the evolution of asteroidal material in space. The main purpose of this study is to modify our previous method for a small amount of sample. Major improvements of the analytical method are as follows: (1) Chemical separation procedure of Sm and Gd, (2) Analytical procedures of a few ng of Sm and Gd isotopes extracted from a few tens mg-sized samples.

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2. EXPERIMENTAL

2.1 Samples

Samples 1F and 2F are test samples from ISAS. Besides the two samples, commercial chemical reagents (Shin-etsu Chemical Co. Ltd., 99.9% grade Sm_2O_3 and Gd_2O_3) and two geological reference rocks JB-1a (basalt from Sasebo, Nagasaki) and JG-1a (granodiorite from Sohri, Gumma) were measured as reference materials for terrestrial standard of Sm and Gd isotopic compositions in order to check the analytical precision and accuracy of a mass spectrometer.

2.2 Chemical procedures

About 100 mg of each sample was divided into two portions, 20 mg for Daly analysis and 50 mg for Faraday analysis. Each sample was digested by HF-HClO_4 . Digestion of JB-1a and JG-1a was done only for Daly analysis. Then, the sample was heated to dryness and re-dissolved in 1 ml of 2M HCl. The sample solution was loaded onto a cation exchange resin column (Bio-rad AG50WX8, 200–400 mesh, H^+ form, $4.0\phi \times 50$ mm) and washed with 4.7 ml of 2M HCl

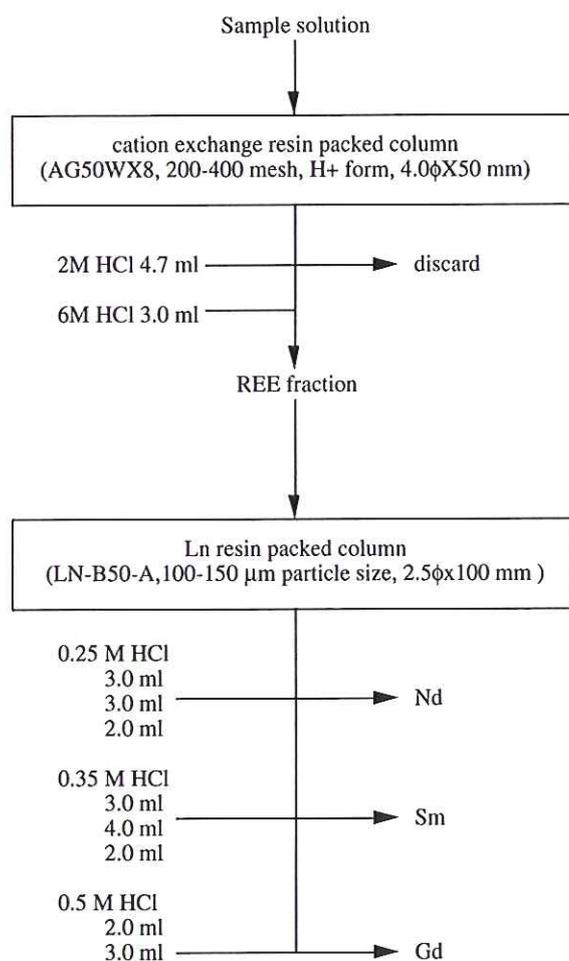


Fig. 1: The scheme of chemical procedures for separation of Nd, Sm and Gd.

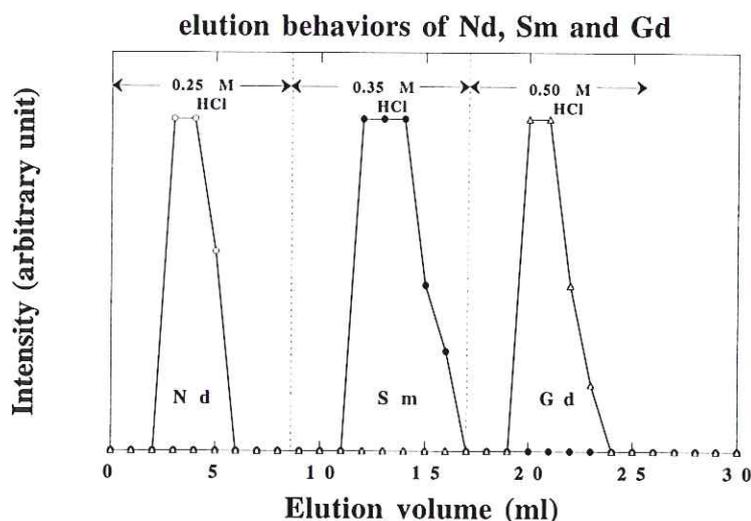


Fig. 2: Elution behaviors of Nd, Sm and Gd by using Ln resin loaded various concentrations of HCl as an eluent.

before REE were eluted with 3 ml of 6M HCl. This REE fraction from the first column was evaporated to dryness and re-dissolved in a drop of 0.1M HCl. The solution was loaded onto a second column packed Ln resin (LN-B50-A produced by Eichrom Industries, Inc., 100–150 μm particle size, $2.5\phi \times 100$ mm) to separate Nd, Sm and Gd by using 0.25M, 0.35M and 0.5M HCl, respectively. The recovery of each element through this procedure is more than 90%. The scheme of the column chemistry and elution curve of Nd, Sm and Gd are illustrated in Figs. 1 and 2.

The advantage of use of Ln resin for REE separation is to be able to use HCl as an eluent. Conventional REE separation method using NH_4^+ formed cation exchange resin with α -hydroxy isobutyric acid (α -HIBA) as an eluent needs complicated processes for the conditioning of the resin and for the purification of α -HIBA (Hidaka et al., 1995). On the other hand, the REE separation using Ln resin is more convenient and simple rather than the conventional method.

2.3 Mass spectrometry

A VG54-30 thermal ionization mass spectrometer was used in this study. The mass spectrometer is equipped with two kinds of detector; seven Faraday cup collectors for simultaneous detection of seven isotopes, and single Daly detector for detection of low intensity of ion beam. We have already developed analytical procedures of precise isotopic determination of Sm and Gd with 0.001% of reproducibilities by use of multi-Faraday cup collectors (Hidaka et al., 1995). In this method, however, more than a few hundreds ng of Sm and Gd are required to detect intense ion beam more than 1.0×10^{-11} A for $^{152}\text{Sm}^+$ and $^{158}\text{Gd}^+$. On the other hand, Daly detector is more sensitive than Faraday cup collector, and often used for isotopic analysis of low intensity of ion beam less than 1×10^{-13} A. However, it is generally known that the analytical accuracy of Daly detector is worse than that of Faraday cup. In this study, in order to check the analytical accuracy of Daly detector, detailed comparison of the isotopic analysis was performed between Daly system and multi-Faraday system.

For Faraday analysis, data collection with static multi-mode is performed under the constant

magnetic field during one isotopic measurement run. Since the mass spectrometer in this study has seven collectors, it is not sufficient to simultaneously measure all seven isotopes of Sm and Gd and their isobaric interferences. Monitoring of isobaric interferences, ^{146}Nd for Sm and ^{161}Gd for Gd, is necessarily required for precise isotopic analyses of Sm and Gd. Therefore, configurations of seven collectors were fixed to ^{146}Nd , ^{147}Sm , ^{148}Sm , ^{149}Sm , ^{150}Sm , and ^{152}Sm for Sm isotopic measurement, and to ^{154}Gd , ^{155}Gd , ^{156}Gd , ^{157}Gd , ^{158}Gd , ^{160}Gd , and ^{161}Dy for Gd. ^{144}Sm and ^{152}Gd isotopes were not measured in this study. On the other hand, Daly analysis is performed by peak jumping mode. Daly analysis needs longer time than Faraday analysis to measure all isotopes of Sm and Gd, because the mass spectrometer has only one Daly detector. The analytical precision by Daly system depends mainly upon a stability of ion beam from emitter. Considering a rapid analytical running by Daly mode, minor isotope ^{152}Gd was excluded from the Daly analytical cycle in this study.

The Sm sample was loaded onto a Re side filament of triple Re filament assembly. 1×10^{-12} A of $^{152}\text{Sm}^+$ ion was detected from 20 ng of Sm chemical reagent. Most previous studies on Gd isotopic measurement have utilized the GdO, since Gd is preferably ionized as GdO^+ rather than Gd^+ (Eugster et al., 1970; Lugmair and Marti, 1971). An oxygen leak into ion source chamber of mass spectrometer is useful to enhance the intensity of the GdO^+ ion beam. In this case, Gd sample is loaded onto a Re center filament of single Re filament assembly. In this study, however, the Gd sample was loaded onto a Re side filament of triple Re filament assembly and measured not as GdO^+ but as Gd^+ without an oxygen leak, because the recalculation of isotopic abundances for Gd from those of GdO is not a simple matter. 1×10^{-12} A of $^{158}\text{Gd}^+$ ion was obtained from 20 ng of Gd chemical reagent.

Table 1a: Daly detector analysis (a) Isotopic composition of Sm

sample	$^{144}\text{Sm}/^{152}\text{Sm}$	$^{148}\text{Sm}/^{152}\text{Sm}$	$^{149}\text{Sm}/^{152}\text{Sm}$	$^{150}\text{Sm}/^{152}\text{Sm}$	$^{154}\text{Sm}/^{152}\text{Sm}$
STD	0.11502	0.42082	0.51748	0.27672	0.85203
	± 3	± 7	± 8	± 6	± 20
JB-1a	0.11470	0.42039	0.51669	0.27618	0.85262
	± 7	± 10	± 18	± 12	± 45
JG-1a	0.11482	0.42092	0.51711	0.27587	0.84885
	± 16	± 17	± 32	± 22	± 79
1F	0.11466	0.41991	0.51664	0.27670	0.85123
	± 22	± 49	± 52	± 25	± 108
2F	0.11474	0.41994	0.51711	0.27584	0.85190
	± 11	± 23	± 30	± 18	± 53

3. RESULTS

Tables 1 and 2 show isotopic data for Sm and Gd collected by Daly detector and Faraday collectors, respectively. Unfortunately Gd isotopic data of 1F using Faraday are not shown because of poor collection of the data due to rapid decay of the ion beam. The uncertainties in the tables are shown as 2σ of the means. Correction for instrumental mass fractionation was performed using an exponential law with normalizing factors with $^{147}\text{Sm}/^{152}\text{Sm}=0.56081$ and $^{155+156}\text{Gd}/^{160}\text{Gd}=1.61290$. Comparison of the isotopic data in Tables 1 and 2 reveals that the analytical precision by Faraday is 3-10 times better than that by Daly. In addition, as a result

Table 1b: Daly detector analysis (b) Isotopic composition of Gd

sample	$^{154}\text{Gd}/^{160}\text{Gd}$	$^{155}\text{Gd}/^{160}\text{Gd}$	$^{157}\text{Gd}/^{160}\text{Gd}$	$^{158}\text{Gd}/^{160}\text{Gd}$
STD	0.09982	0.67561	0.71649	1.1349
	± 4	± 12	± 8	± 2
JB-1a	0.09997	0.67513	0.71754	1.1385
	± 12	± 52	± 31	± 7
JG-1a	0.09985	0.67554	0.71580	1.1372
	± 30	± 35	± 26	± 7
1F	0.10007	0.67495	0.71554	1.1354
	± 22	± 151	± 76	± 14
2F	0.10005	0.67731	0.71680	1.1359
	± 25	± 97	± 75	± 21

Table 2a: Faraday cup analysis(a) Isotopic composition of Sm

sample	$^{148}\text{Sm}/^{152}\text{Sm}$	$^{149}\text{Sm}/^{152}\text{Sm}$	$^{150}\text{Sm}/^{152}\text{Sm}$	$^{154}\text{Sm}/^{152}\text{Sm}$
STD	0.420461	0.516886	0.275990	0.850854
	± 5	± 5	± 2	± 5
1F	0.420449	0.516941	0.276013	0.851263
	± 73	± 62	± 80	± 108
2F	0.420448	0.516801	0.275977	0.850897
	± 125	± 139	± 98	± 183

Table 2b: Faraday cup analysis(b) Isotopic composition of Gd

sample	$^{154}\text{Gd}/^{160}\text{Gd}$	$^{155}\text{Gd}/^{160}\text{Gd}$	$^{157}\text{Gd}/^{160}\text{Gd}$	$^{158}\text{Gd}/^{160}\text{Gd}$
STD	0.099750	0.676983	0.715887	1.135825
	± 1	± 5	± 4	± 5
2F	0.099900	0.676903	0.715880	1.135792
	± 125	± 183	± 181	± 199

of several measurements of standard samples, the analytical accuracy by Faraday is better than that of Daly. Therefore, it can be concluded that Faraday analysis provides more reliable isotopic data than Daly analysis even for a few tens ng of Sm and Gd. As shown in Table 2, the Sm isotopic data of 1F and 2F, and the Gd isotopic data of 2F are agreement with those of Sm and Gd chemical reagents (STD in Table 2) which have no record of neutron-irradiation, respectively.

There are several methods of estimating the cosmic-ray-induced neutron fluence values Ψ from the Sm and Gd isotopic shifts (Hidaka et al., 2000a; 200b; Eugster et al., 1970). In this report, Ψ was calculated from the comparison of the Sm isotopic shifts between experimentally neutron-irradiated materials and samples (Hidaka et al., 1995; 1999; 2000a; 200b). The results are summarized in Table 3. The present analytical method using Faraday collectors can detect effects caused by neutron fluence of 1×10^{14} neutrons/cm² which corresponds to 2 Ma of cosmic-ray exposure duration of the surface of chondritic body. The estimated neutron fluences of 1F

Table 3: Information of neutron capture effects

sample	$^{150}\text{Sm}/^{149}\text{Sm}$	$^{158}\text{Gd}/^{160}\text{Gd}$	Ψ ($\times 10^{15}$ n/cm 2)*	Exposure age (Ma)**
STD	0.533948 \pm 6	1.58660 \pm 1		
1F	0.533935 \pm 167	Not analyzed	0 ± 2.16	<20
2F	0.534010 \pm 237	1.58656 \pm 49	0.80 ± 3.06	<30

*Neutron fluence Ψ was calculated from the comparison of the Sm isotopic shifts between experimentally neutron-irradiated materials (Hidaka et al., 1995) and samples.

**Exposure age was estimated from the correlation between Ψ and exposure ages in some chondritic meteorites (Hidaka et al., 2000a).

and 2F from the Sm isotopic deviations are $(0 \pm 2.16) \times 10^{15}$ and $(0.80 \pm 3.06) \times 10^{15}$ n/cm 2 , respectively. The data for major and some minor chemical components of sample is required to estimate cosmic-ray exposure duration from the neutron fluence (Liegenfelter et al., 1972; Spergel et al., 1986). Assuming the samples 1F and 2F have similar chemical component to ordinary chondrites, the neutron fluences of 1F and 2F correspond to <20 Ma and <30Ma of exposure ages, respectively. In order to perform higher precision analysis of Sm and Gd isotopes for small amount of samples, detection of larger intensity of ion beam is essential. For example of a mass spectrometric technique, it is well known that co-loaded silica gel and phosphoric acid with Sr is an efficient activator to enhance Sr ion intensity in a mass spectrometer. We are now looking for any activated materials for Sm and Gd isotopic analyses to enhance the ion beam intensity for small amount of sample.

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